ON THE TWO-CENTER EXCHANGE INTEGRALS*

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In a recent discussion[1] it was shown that the two-center exchange integrals are most conveniently expressed in terms of certain auxiliary functions, $B_j^{M\Omega}(\beta)$ and $\phi_{n\bar{n}}^{M\Omega}(\alpha,\bar{\alpha})$. Of these, the functions $\phi_{n\bar{n}}^{M\Omega}$ are the more complicated ones, and it was felt that a condensed account of the recurrence method of their computation would be useful. In the following this method is therefore presented in the form of an instruction for actual work. At the same time, some minor modifications have been made.

First step: Compute the functions

$$A_0(\alpha),\ A_1(\alpha),\ A_2(\alpha),\ \ldots\ A_N(\alpha)\ ;$$

$$A_0(\bar{\alpha}),\ A_1(\bar{\alpha}),\ A_2(\bar{\alpha}),\ \ldots\ A_{\bar{N}}(\bar{\alpha})\ ;$$

$$A_0(\alpha+\bar{\alpha}),\ A_1(\alpha+\bar{\alpha}),\ A_2(\alpha+\bar{\alpha}),\ \ldots\ A_{N+\bar{N}}(\alpha+\bar{\alpha})\ ;$$

by means of the recurrence procedure

$$A_0(x) = e^{-x}/x, \quad A_n(x) = (1/x)\left[nA_{n-1}(x) + e^{-x}\right].$$

For the arguments: $x = 0.25, 0.5, 0.75, \ldots$, the value of $A_n(x)$

[1] Cf. K. Rüdenberg, J. Chem. Phys., 19, 1459 (1951).

can be taken from Kotani's Table.

The values of the highest indices, i.e., N, $\bar{N}$, are determined by the recurrence procedure which follows.

Second step: Compute the functions

$$G_0(\alpha),\ G_1(\alpha),\ G_2(\alpha),\ \ldots\ G_N(\alpha)\ ;$$

$$G_0(\bar{\alpha}),\ G_1(\bar{\alpha}),\ G_2(\bar{\alpha}),\ \ldots\ G_{\bar{N}}(\bar{\alpha})\ ;$$

$$G_0(\alpha+\bar{\alpha}),\ G_1(\alpha+\bar{\alpha}),\ G_2(\alpha+\bar{\alpha}),\ \ldots\ G_{N+\bar{N}}(\alpha+\bar{\alpha})\ ;$$

by means of the recurrence procedure

$$G_0(x) = \tfrac{1}{2}e^{-x}\left[C + \log 2x - e^{2x}\mathrm{Ei}(-2x)\right],$$

$$G_1(x) = \tfrac{1}{2}e^{-x}\left[C + \log 2x + e^{2x}\mathrm{Ei}(-2x)\right],$$

$$G_n(x) = G_{n-2}(x) - A_{n-2}(x)\ .$$

For the argument values: $x = 0.25,\ 0.5,\ 0.75,\ \ldots,$ the functions $f_0(0,x)$, $f_0(1,x)$, of Kotani's Table can be used in order to calculate G_0 and G_1 according to

$$G_0(x) = xf_0(0,x),\quad G_1(x) = xf_0(1,x) - f_0(0,x)\ .$$

Third step: Compute the functions

$$\phi^{00}_{n\bar{n}}(\alpha,\bar{\alpha}) = \phi_{n\bar{n}}(\alpha,\bar{\alpha})\ ,$$

for $n = 0, 1, 2, \ldots N$; $\bar{n} = 0, 1, 2, \ldots \bar{N}$, in the following way. First draw the skeleton of rules of the table shown in Fig. 1 (the diagonal lines preferably in a different color) and enter the values for all functions except the functions $\phi_{n\bar{n}}$. Then compute and enter successively the latter using the recurrence formulae:

$$\phi_{n\bar{n}} = (1/\alpha\bar{\alpha}) \Big\{ \bar{\alpha} n \;\; \phi_{n-1,\bar{n}} + e^{-\bar{\alpha}} G_n(\alpha)$$
$$+ \alpha\bar{n} \;\; \phi_{n,\bar{n}-1} + e^{-\alpha} G_{\bar{n}}(\bar{\alpha})$$
$$- n\bar{n} \;\; \phi_{n-1,\bar{n}-1} - G_{n+\bar{n}}(\alpha + \bar{\alpha}) \Big] .$$

If $n = 0$ or $\bar{n} = 0$, or if both are zero, then the terms on the right hand side which are multiplied by zero have simply to be omitted. Each $\phi_{n\bar{n}}$ is obtained by one operation (on a calculating machine permitting accumulative multiplication) following a simple geometrical path in the table.

<u>Fourth step</u>: Compute the functions $A_{n\bar{n}}(\alpha,\bar{\alpha})$. First draw the skeleton of rules of Figure 2 and enter the values for all functions except the functions $A_{n\bar{n}}$. Then compute and enter successively the latter using the recurrence formulae:

$$A_{n\bar{n}} = (1/\alpha + \bar{\alpha}) \left[nA_{n-1,\bar{n}} + \bar{n}A_{n,\bar{n}-1} + A_n(\alpha) \; A_{\bar{n}}(\bar{\alpha}) \right] .$$

For $n = 0$ or $\bar{n} = 0$, or both $= 0$, the terms containing the factor zero have to be omitted. Each $A_{n\bar{n}}$ is obtained by one operation (on a calculating machine permitting accumulative multiplication) following a simple geometrical path in the table.

<u>Fifth step</u>: Compute the functions $\phi^{01}_{n\bar{n}}(\alpha,\bar{\alpha})$ and $\phi^{02}_{n\bar{n}}(\alpha,\bar{\alpha})$ by means of the recurrence formulae:

$$\phi^{01}_{n\bar{n}}(\alpha,\bar{\alpha}) = \phi^{00}_{n+1,\bar{n}+1}(\alpha,\bar{\alpha}) - A_n(\alpha)A_{\bar{n}}(\bar{\alpha}) - A_{n\bar{n}}(\alpha,\bar{\alpha}) ,$$

$$4 \; \phi^{02}_{n\bar{n}}(\alpha,\bar{\alpha}) = 9 \; \phi^{01}_{n+1,\bar{n}+1}(\alpha,\bar{\alpha}) + \phi^{00}_{n\bar{n}}(\alpha,\bar{\alpha})$$
$$+ 3 \left[A_n(\alpha)A_{\bar{n}+1}(\bar{\alpha}) + A_{n+1}(\alpha)A_{\bar{n}}(\bar{\alpha}) \right]$$
$$- 3 \left[\phi^{00}_{n+2,\bar{n}}(\alpha,\bar{\alpha}) + \phi^{00}_{n,\bar{n}+2}(\alpha,\bar{\alpha}) \right]$$
$$- 3 \left[A_n(\alpha)A_{\bar{n}}(\bar{\alpha}) + A_{n\bar{n}}(\alpha,\bar{\alpha}) \right] .$$

<u>Sixth step</u>: Compute the functions $\phi^{03}_{n\bar{n}}$, $\phi^{04}_{n\bar{n}}$, . . . $\phi^{0\ell}_{n\bar{n}}$ by means of the recurrence formulae:

$$9\ \phi^{03}_{n\bar{n}} = 25\ \phi^{02}_{n+1,\bar{n}+1} + 9\ \phi^{01}_{n\bar{n}} + 5\ \phi^{00}_{n+1,\bar{n}+1} - 15\left[\phi^{01}_{n+2,\bar{n}} + \phi^{01}_{n,\bar{n}+2}\right],$$

$$\begin{aligned}\ell^2(2\ell-5)\ \phi^{0,\ell}_{n\bar{n}} = {} & (2\ell-5)(2\ell-1)^2\ \phi^{0,\ell-1}_{n+1,\bar{n}+1} \\ & + \left[(2\ell-5)(\ell-1)^2 + (2\ell-1)(\ell-2)^2\right]\phi^{0,\ell-2}_{n\bar{n}} \\ & + (2\ell-1)(2\ell-5)^2\ \phi^{0,\ell-3}_{n+1,\bar{n}+1} \\ & - (2\ell-1)(2\ell-3)(2\ell-5)\left[\phi^{0,\ell-2}_{n+2,\bar{n}} + \phi^{0,\ell-2}_{n,\bar{n}+2}\right] \\ & - (2\ell-1)(\ell-3)^2\ \phi^{0,\ell-4}_{n\bar{n}} .\end{aligned}$$

The second formula is valid for all $\ell \geq 4$.

<u>Seventh step</u>: Compute the functions $\phi^{M\ell}_{n\bar{n}}(\alpha,\bar{\alpha})$ for $M = 1,2,$ . . . by means of the recurrence formulae:

$$\phi^{M+1,\ell}_{n\bar{n}} = \phi^{M,\ell}_{n+1,\bar{n}+1} - \frac{(\ell+M)}{(2\ell+1)}\ \phi^{M,\ell-1}_{n\bar{n}} - \frac{(\ell+1-M)}{(2\ell+1)}\ \phi^{M,\ell+1}_{n\bar{n}} .$$

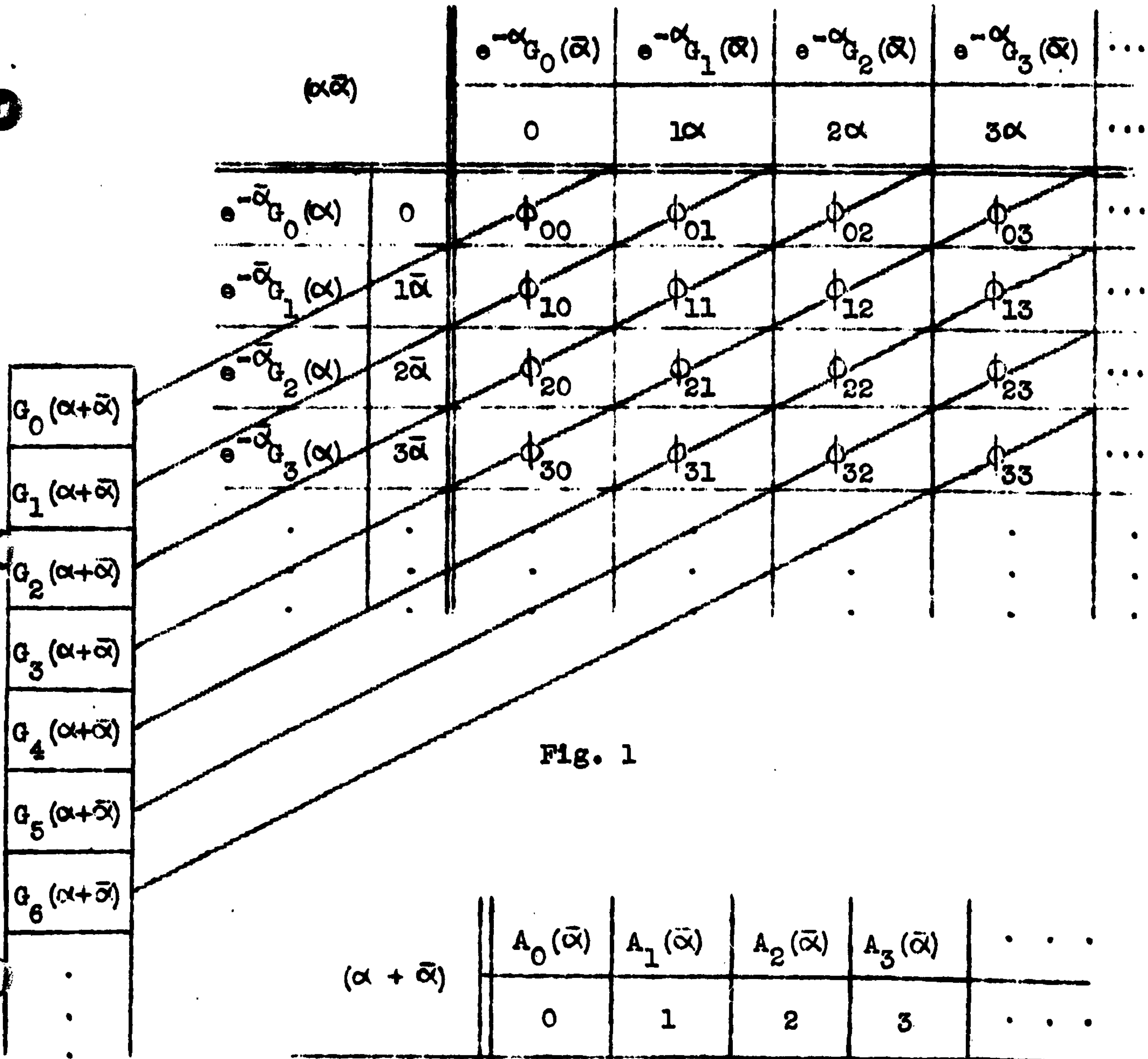

Fig. 1

$(\alpha+\bar{\alpha})$		$A_0(\bar{\alpha})$	$A_1(\bar{\alpha})$	$A_2(\bar{\alpha})$	$A_3(\bar{\alpha})$	. . .
		0	1	2	3	. . .
$A_0(\alpha)$	0	A_{00}	A_{01}	A_{02}	A_{03}	. . .
$A_1(\alpha)$	1	A_{10}	A_{11}	A_{12}	A_{13}	. . .
$A_2(\alpha)$	2	A_{20}	A_{21}	A_{22}	A_{23}	. . .
$A_3(\alpha)$	3	A_{30}	A_{31}	A_{32}	A_{33}	. . .
⋮	⋮	⋮	⋮	⋮	⋮	⋮

Fig. 2